

Application No.: 10/777,562
Response dated: November 30, 2005
Reply to Office Action November 21, 2005

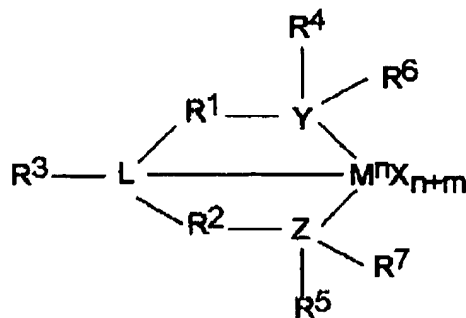
Please amend the Claims as follows:

1. (Currently Amended) A process for polymerizing olefin(s) comprising combining said olefin(s) in the presence of a catalyst system comprising a Group 15 containing bidentate or tridentate ligated hafnium catalyst compound wherein the hafnium metal atom is bound to at least one leaving group and to at least two Group 15 atoms, wherein the at least one of the at least two Group 15 atoms is bound to a Group 15 or 16 atom through a bridging group, and a [bulky ligand metallocene-type] metallocene catalyst compound wherein metallocene compound and said Group 15 containing bidentate or tridentate ligated hafnium catalyst compound are added to a polymerization reactor in one of a slurry, a solution, an emulsion, a dispersion or a suspension.
2. (Original) The process of claim 1 wherein the bridging group is selected from the group consisting of a C₁ to C₂₀ hydrocarbon group, a heteroatom containing group, silicon, germanium, tin, lead, and phosphorus.
3. (Original) The process of claim 2 wherein the Group 15 or 16 atom may also be bound to nothing, a hydrogen, a Group 14 atom containing group, a halogen, or a heteroatom containing group, and wherein each of the two Group 15 atoms are also bound to a cyclic group and may optionally be bound to hydrogen, a halogen, a heteroatom or a hydrocarbyl group, or a heteroatom containing group.
4. (Original) The process of claim 1 wherein the Group 15 containing hafnium compound is represented by the formulae:

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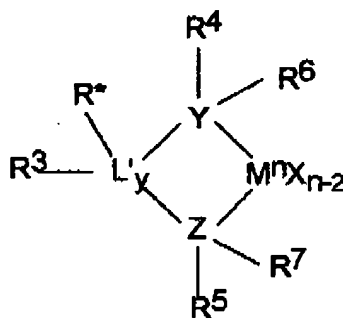
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Formula (I)

or



Formula (II)

wherein M is hafnium;

each X is independently a leaving group;

y is 0 or 1;

n is the oxidation state of M;

m is the formal charge of the Y, Z and L or the Y, Z and L' ligand;

L is a Group 15 or 16 element;

L' is a Group 15 or 16 element or Group 14 containing group;

Y is a Group 15 element;

Z is a Group 15 element;

R¹ and R² are independently a C₁ to C₂₀ hydrocarbon group, a heteroatom containing group having up to twenty carbon atoms, silicon, germanium, tin, lead, or phosphorus;

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R^3 is absent or a hydrocarbon group, hydrogen, a halogen, a heteroatom containing group;

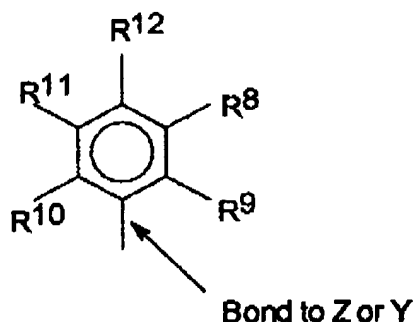
R^4 and R^5 are independently an alkyl group, an aryl group, substituted aryl group, a cyclic alkyl group, a substituted cyclic alkyl group, a cyclic arylalkyl group, a substituted cyclic arylalkyl group or multiple ring system;

R^1 and R^2 may be interconnected to each other, and/or R^4 and R^5 may be interconnected to each other;

R^6 and R^7 are independently absent, or hydrogen, an alkyl group, halogen, heteroatom or a hydrocarbonyl group; and

R^* is absent, or is hydrogen, a Group 14 atom containing group, a halogen, a heteroatom containing group.

5. (Original) The process of claim 4 wherein R^4 and R^5 are represented by the formula:



wherein R^8 to R^{12} are each independently hydrogen, a C_1 to C_{40} alkyl group, a halide, a heteroatom, a heteroatom containing group containing up to 40 carbon atoms, wherein any two R groups may form a cyclic group and/or a heterocyclic group and wherein the cyclic groups may be aromatic.

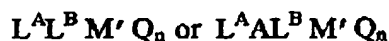
6. (Currently Amended) The process of claim 5 wherein R^8 to R^{12} [R^9 , R^{10} and R^{12}] are independently a methyl, ethyl, propyl or butyl group.
7. (Currently Amended) The process of claim 5 wherein R^8 to R^{12} [R^9 , R^{10} and R^{12}] are methyl groups[, and R^8 and R^{11} are hydrogen].

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8. (Original) The process of claim 4 wherein L, Y, and Z are nitrogen, R¹ and R² are a hydrocarbon radical, R³ is hydrogen, and R⁶ and R⁷ are absent.
9. (Original) The process of claim 4 wherein L and Z are nitrogen, L' is a hydrocarbyl radical, and R⁶ and R⁷ are absent.
10. (Original) The process of claim 1 wherein the catalyst system is supported on a carrier.
11. (Original) The process of claim 1 wherein the process is a continuous gas phase process.
12. (Original) The process of claim 1 wherein the process is a continuous slurry phase process.
13. (Original) The process of claim 1 wherein the olefin(s) is ethylene.
14. (Original) The process of claim 1 wherein the olefins are ethylene and at least one other monomer having from 3 to 20 carbon atoms.
15. (Original) The process of claim 1 wherein the catalyst system further comprises an activator.
16. (New) The process of claim 1, 4 or 5, wherein the metallocene catalyst compound comprises a metallocene compound of the general formula:



wherein M' is a Group 4, 5 or 6 metal atom,

L^A and L^B are selected from the group consisting of cyclopentadienyl,

tetrahydroindenyl, indenyl, fluorenyl, and substituted versions thereof, L^A and L^B are each bonded to M' ;

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each Q is a monoanionic leaving group,

A is a divalent bridging group containing at least one Group 13 to Group 16 atom; and

n is 0, 1 or 2.

17. (New) The process of claim 16 wherein M' is a Group 4 metal, and wherein said process is a gas phase process.
18. (New) The process of claim 1 wherein the Group 15 containing bidentate or tridentate ligated hafnium compound and the metallocene catalyst compound are present in a molar ratio of 1:99 to 99:1.
19. (New) The process of claim 1 wherein the Group 15 containing bidentate or tridentate ligated hafnium compound and the metallocene catalyst compound are present in a molar ratio of 80:20 to 20:80.
20. (New) The process of claim 1, wherein said Group 15 containing bidentate or tridentate ligated hafnium compound comprises a tridentate ligated group, wherein said metallocene catalyst compound is represented by the formulae:



where M' is a Group 4, 5, or 6 metal atom; L^A and L^B, comprise unsubstituted or substituted, cyclopentadienyl ligands or cyclopentadienyl-type ligands, heteroatom substituted and/or heteroatom containing cyclopentadienyl ligands bonded to M', L^A and L^B may be the same or different, L^A and L^B are each bonded to M'; Q is a monoanionic ligand, n is 0, 1 or 2, such that formula (III) represents a neutral metallocene catalyst compound; wherein said process further comprises combining an activator selected from alumoxane, a modified alumoxane, non-coordinating ionic activators, non-coordinating neutral activators, and combinations thereof; and wherein said process is a gas phase process.

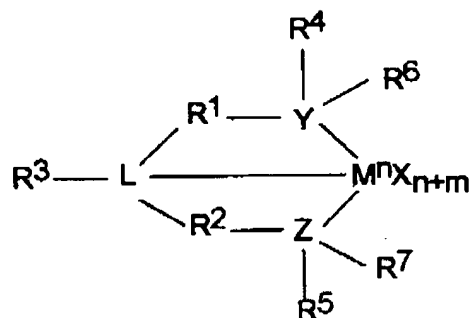
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21. (New) The process of claim 15, wherein said activator is selected from alumoxane, modified alumoxane, or combinations thereof, and said process further comprises combining said catalysts and the activator depositing on, contacting with, vaporized with, bonded to, incorporating within, adsorbing in, or absorbing in, a support.
22. (New) The process of claim 21, wherein said olefin(s) comprise one or more of ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1, decene-1, or combinations thereof.
23. (New) The process of claim 20, wherein said olefin(s) comprise one or more of ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1, decene-1, or combinations thereof.
24. (New) The process of claim 22, wherein said olefin(s) comprise one or more of ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1, or combinations thereof.
25. (New) The process of claim 23, wherein said olefin(s) comprise one or more of ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1, or combinations thereof.
26. (New) The process of claims 1 or 20, wherein said Group 15 containing bidentate or tridentate ligated hafnium compound is a tridentate compound represented by the formulae:

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wherein

M is hafnium.

each X is independently a leaving group,

n is the oxidation state of M ,

m is the formal charge of the ligand comprising Y, Z and L,

L is a Group 15 element,

Y is a Group 15 element,

Z is a Group 15 element,

R¹ and R² are independently a C₁ to C₂₀ hydrocarbon group, or a heteroatom

containing group having up to twenty carbon atoms, the heteroatom

selected from the group consisting of silicon, germanium, tin, lead, and

phosphorus; wherein optionally, R¹ and R² are interconnected to each

other, and/or R⁴ and R⁵ may be interconnected to each other,

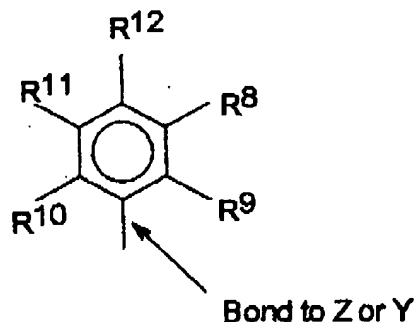
R³ is absent, a hydrocarbon group, a hydrogen, a halogen, or a heteroatom containing group,

wherein R⁴ and R⁵ are represented by the formula

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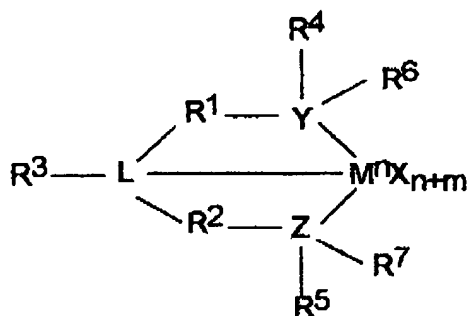
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wherein

R^8 to R^{12} are each independently hydrogen, a C_1 to C_{40} alkyl group, a halide, a heteroatom, a heteroatom containing group containing up to 40 carbon atoms, wherein any two R groups may form a cyclic group and/or a heterocyclic group, and wherein the cyclic groups may be aromatic, and R^6 and R^7 are independently absent, hydrogen, an alkyl group, halogen, heteroatom or a hydrocarbyl group.

27. (New) The process of claim 16, wherein said Group 15 containing bidentate or tridentate ligated hafnium compound is a tridentate compound represented by the formulae:



wherein

M is hafnium,

each X is independently a leaving group,

n is the oxidation state of M,

m is the formal charge of the ligand comprising Y, Z and L,

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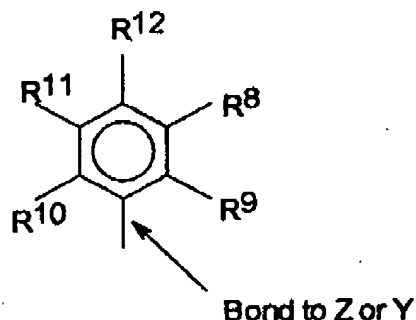
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L is a Group 15 element,

Y is a Group 15 element,

Z is a Group 15 element,

R¹ and R² are independently a C₁ to C₂₀ hydrocarbon group, or a heteroatom containing group having up to twenty carbon atoms, the heteroatom selected from the group consisting of silicon, germanium, tin, lead, and phosphorus; wherein optionally, R¹ and R² are interconnected to each other, and/or R⁴ and R⁵ may be interconnected to each other, R³ is absent, a hydrocarbon group, a hydrogen, a halogen, or a heteroatom containing group, wherein R⁴ and R⁵ are represented by the formula



wherein

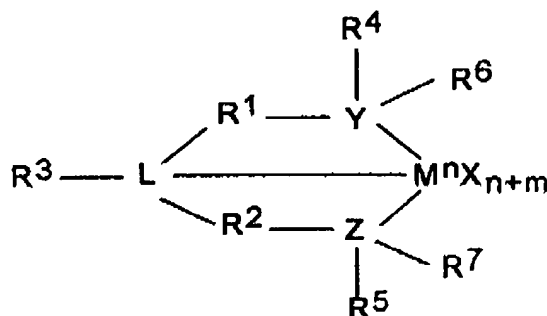
R⁸ to R¹² are each independently hydrogen, a C₁ to C₄₀ alkyl group, a halide, a heteroatom, a heteroatom containing group containing up to 40 carbon atoms, wherein any two R groups may form a cyclic group and/or a heterocyclic group, and wherein the cyclic groups may be aromatic, and R⁶ and R⁷ are independently absent, hydrogen, an alkyl group, halogen, heteroatom or a hydrocarbyl group.

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28. (New) The process of claims 1 or 20, wherein said Group 15 containing bidentate or tridentate ligated hafnium compound is a tridentate compound represented by the formulae:



where M is hafnium, each X is independently an alkyl leaving group, n is the oxidation state of M,

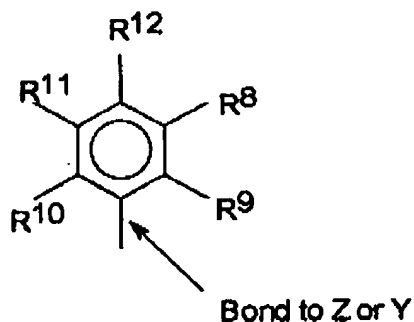
m is the formal charge of the ligand comprising Y, Z and L,

L, Y and Z are nitrogen,

R¹ and R² are independently —CH₂—CH₂—,

R³ is hydrogen,

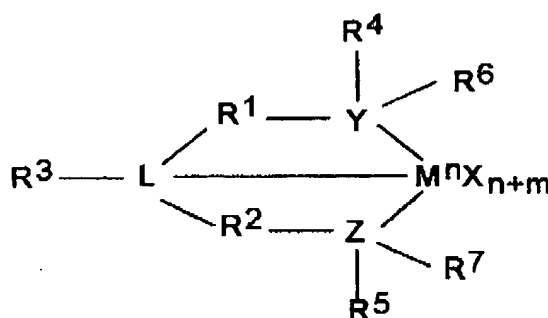
wherein R⁴ and R⁵ are represented by the formula



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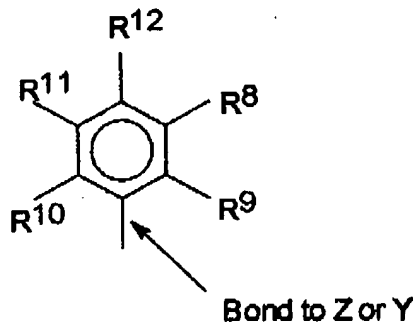
wherein
 R^8 to R^{12} are methyl groups; and
 R^6 and R^7 are absent.

29. (New) The process of claims 16, wherein said Group 15 containing bidentate or tridentate ligated hafnium compound is a tridentate compound represented by the formulae:



where M is hafnium, each X is independently an alkyl leaving group, n is the oxidation state of M,
 m is the formal charge of the ligand comprising Y, Z and L,
 L, Y and Z are nitrogen,
 R^1 and R^2 are independently $-\text{CH}_2-\text{CH}_2-$,
 R^3 is hydrogen,
 wherein R^4 and R^5 are represented by the formula

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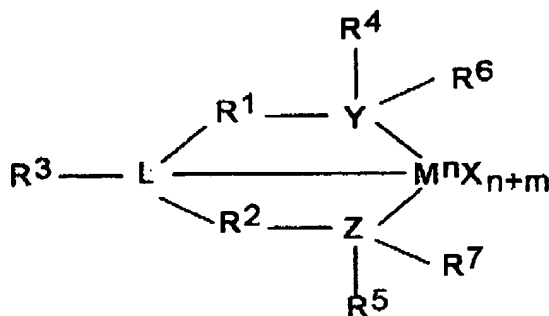


wherein

R⁸ to R¹² are methyl groups; and

R⁶ and R⁷ are absent.

30. (New) The process of claims 1 or 20, wherein said process further comprises producing a polymer from said polymerization of olefin(s), said polymer comprising an ethylene polymer or copolymer comprising a residual metal content of 5.0 ppm or less, an I₂ of from 0.01 to 10 dg/min., an I₂₁ of from 1 to 10dg/min., a density from 0.930 to 0.970 g/cm³, Mw/Mn of between 20 and 60, and a I₂₁/I₂ greater than or equal to 80.
31. (New) A process for polymerizing olefin(s) comprising, combining said olefin(s), a hafnium catalyst compound represented by the formulae:



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where M is hafnium, each X is independently an alkyl leaving group, n is the oxidation state of M,

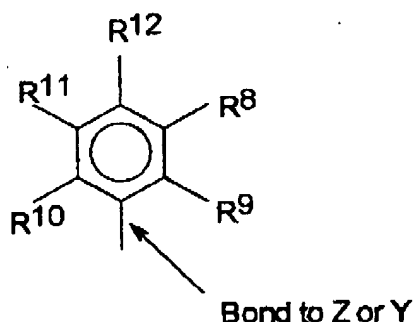
m is the formal charge of the ligand comprising Y, Z and L,

L, Y and Z are nitrogen,

R¹ and R² are independently —CH₂—CH₂—,

R³ is hydrogen,

wherein R⁴ and R⁵ are represented by the formula



wherein

R⁸ to R¹² are methyl groups;

R⁶ and R⁷ are absent;

wherein the metallocene catalyst compound comprises compound of the general formula:



where M' is a Group 4, 5, or 6 metal atom; L^A and L^B comprise unsubstituted or substituted, cyclopentadienyl ligands or cyclopentadienyl-type ligands, heteroatom substituted and/or heteroatom containing cyclopentadienyl ligands bonded to M', L^A and L^B may be the same or different, L^A and L^B are each bonded to M'; Q is a monoanionic ligand, n is 0, 1 or 2, such that formula (III) represents a neutral metallocene catalyst compound;

wherein said process further comprises combining said hafnium catalyst compound and said metallocene catalyst compound, and an alumoxane; wherein

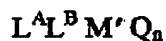
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said hafnium catalyst compound, said metallocene catalyst compound, and said alumoxane are added to a polymerization reactor in one of a slurry, a solution, an emulsion, a dispersion or a suspension;

wherein said olefin(s) comprise one or more of ethylene, butene-1, hexene-1, octene-1, or combinations thereof; and

wherein said process further comprises producing a polymer from said polymerization of olefin(s), said polymer comprising an ethylene polymer or copolymer comprising a residual metal content of 5.0 ppm or less, an I_2 of from 0.01 to 10 dg/min., an I_{21} of from 1 to 10dg/min., a density from 0.930 to 0.970 g/cm³, Mw/Mn of between 20 and 60, and a I_{21}/I_2 greater than or equal to 80.

32. (New) The process of claim 31, wherein said hafnium catalyst compound, said metallocene catalyst compound, said alumoxane and a support are spray dried.
33. (New) A process for polymerizing olefin(s) comprising, combining olefin(s), a catalyst composition having a Group 15 containing tridentate ligated hafnium catalyst compound wherein the hafnium is bound to at least one leaving group and to at least two Group 15 atoms, and wherein at least one of the at least two Group 15 atoms is bound to a group 15 or 16 atom through a bridging group; and a metallocene catalyst compound, wherein said metallocene compound is represented by the formula:



wherein M' is a Group 4, 5 or 6 metal atom;

L^A and L^B are selected from the group consisting of cyclopentadienyl, tetrahydroindenyl, indenyl, fluorenyl, and substituted versions thereof, L^A and L^B are each bonded to M' ;

Q is a monoanionic leaving group;

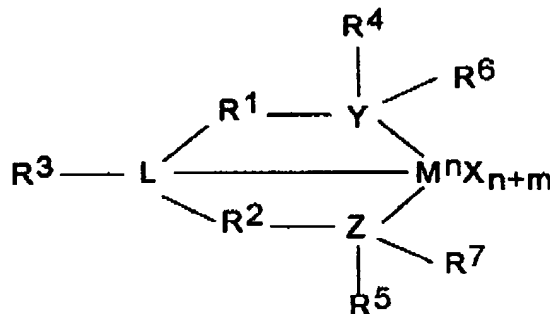
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n is 0, 1 or 2,

wherein said process further comprises combining an activator selected from alumoxane, a modified alumoxane, non-coordinating ionic activators, non-coordinating neutral activators, and combinations thereof; and

wherein said hafnium catalyst compound and said metallocene catalyst compound are added to a polymerization reactor in one of a slurry, a solution, an emulsion, a suspension or a dispersion.

34. (New) The process of claim 33, wherein said hafnium catalyst compound and said metallocene catalyst compound, activator and a support are spray dried.
35. (New) The process of claim 33, wherein said hafnium catalyst compound is represented by the formulae:



where M is hafnium, each X is independently an alkyl leaving group, n is the oxidation state of M,

m is the formal charge of the ligand comprising Y, Z and L,

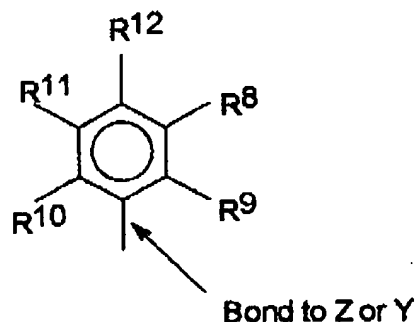
L, Y and Z are nitrogen,

R¹ and R² are independently —CH₂—CH₂—,

R³ is hydrogen,

wherein R⁴ and R⁵ are represented by the formula

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wherein

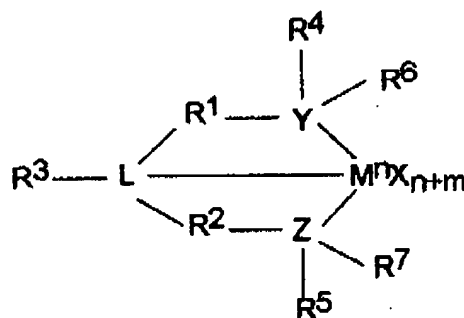
R⁸ to R¹² are methyl groups; and

R⁶ and R⁷ are absent.

36. (New) The process of claim 35, wherein said olefin(s) comprise one or more of ethylene, butene-1, hexene-1, octene-1, or combinations thereof; and wherein said process further comprises producing a polymer from said polymerization of olefin(s), said polymer comprising an ethylene polymer or copolymer comprising a residual metal content of 5.0 ppm or less, an I₂ of from 0.01 to 10 dg/min., an I₂₁ of from 1 to 10dg/min., a density from 0.930 to 0.970 g/cm³, Mw/Mn of between 20 and 60, and a I₂₁/I₂ greater than or equal to 80.
37. (New) The process of claim 36, wherein said Group 15 containing bidentate or tridentate ligated hafnium catalyst compound and said metallocene catalyst compound are present in said polymerization reactor in a molar ratio of 20:80 to 80:20, and wherein said process further comprises adding an aluminum mono, di, or tri, stearate, aluminum octoates, aluminum oleates, or cyclohexylbutyrates, to said process.
38. (New) The process of claim 36, wherein said process is a gas phase process.

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39. (New) A polymerization process comprising, combining ethylene and one or more other olefin(s), a Group 15 containing tridentate ligated hafnium catalyst compound and a metallocene catalyst compound, and an activator, said Group 15 containing tridentate ligated hafnium catalyst compound represented by the formula:



wherein

M is hafnium,

each X is independently a leaving group

n is the oxidation state of M,

m is the formal charge of the Y, Z and L

L is a Group 15 or 16 element,

Y is a Group 15 element,

Z is a Group 15 element,

R¹ and R² are independently a C₁ to C₂₀ hydrocarbon group, a heteroatom containing group having up to twenty carbon atoms, silicon, germanium, tin, lead, or phosphorus,

R³ is absent or a hydrocarbon group, hydrogen, a halogen, a heteroatom containing group,

R⁴ and R⁵ are independently an alkyl group, an aryl group, substituted aryl group, a cyclic alkyl group, a substituted cyclic alkyl group, a cyclic arylalkyl group, a substituted cyclic arylalkyl group or multiple ring system,

interconnected to each other, and

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R^6 and R^7 are independently absent, or hydrogen, an alkyl group, halogen, heteroatom or a hydrocarbyl group; and
said hafnium catalyst compound and said metallocene catalyst compound are added to a polymerization reactor in one of a slurry, a solution, an emulsion, a dispersion or a suspension.

40. (New) The process of claim 39, wherein said activator is selected from alumoxane, a modified alumoxane, non-coordinating ionic activators, non-coordinating neutral activators, and combinations thereof, and said process further comprising combining said catalysts and the activator depositing on, contacting with, vaporized with, bonded to, incorporating within, adsorbing in, or absorbing in, a support.
41. (New) The process of claim 40, wherein said olefin(s) comprise one or more of ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1, decene-1, or combinations thereof; wherein said process further comprises producing a polymer from said polymerization of olefin(s), and said polymer comprising an ethylene polymer or copolymer comprising a residual metal content of 5.0 ppm or less, an I_2 of from 0.01 to 10 dg/min., an I_{21} of from 1 to 10 dg/min., a density from 0.930 to 0.970 g/cm³, M_w/M_n of between 20 and 60, and a I_{21}/I_2 greater than or equal to 80.
42. (New) The process of claim 41, wherein said wherein the metallocene compound comprises the general formula:



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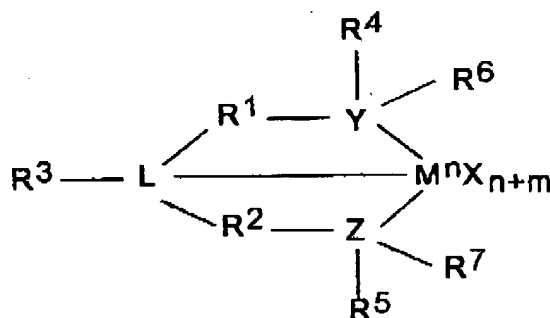
wherein M' is a Group 4, 5 or 6 metal atom,

L^A and L^B are selected from the group consisting of cyclopentadienyl, tetrahydroindenyl, indenyl, fluorenyl, and substituted versions thereof, L^A and L^B are each bonded to M' ;

each Q is a monoanionic leaving group; and

n is 0, 1 or 2.

43. (New) The process of claims 42, wherein said Group 15 containing tridentate ligated hafnium catalyst compound is represented by the formulae:



where M is hafnium, each X is independently an alkyl leaving group, n is the oxidation state of M ,

m is the formal charge of the ligand comprising Y , Z and L ,

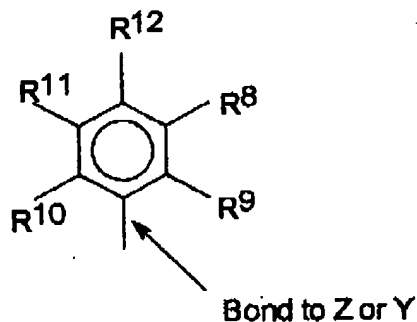
L , Y and Z are nitrogen,

R^1 and R^2 are independently $-\text{CH}_2-\text{CH}_2-$,

R^3 is hydrogen, and

wherein R^4 and R^5 are represented by the formula

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wherein

R⁸ to R¹² are methyl groups;

R⁶ and R⁷ are absent.

44. (New) The process of claim 43, wherein said Group 15 containing tridentate ligated hafnium catalyst compound and said metallocene catalyst compound are present in said polymerization reactor in a molar ratio of 20:80 to 80:20 and wherein said process further comprises adding an aluminum mono, di, or tri, stearate, aluminum octoates, aluminum oleates, or cyclohexylbutyrates, to said process.
45. (New) the process of claim 44, wherein said hafnium catalyst compound, said metallocene catalyst compound, said activator and said support are spray dried, and wherein said process is a gas phase process.